

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CDTE FILMS OBTAINED BY LASER ABLATION

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ABSTRACT

A simple and cheap method has been developed for the deposition of cadmium telluride thin films on glass substrates by pulsed Nd:YAG laser evaporation of cadmium telluride pellets prepared from high purity Cd and Te powders. Preliminary characterization of the crystallographic, electrical and optical properties of the films has been performed as a function of the deposition conditions (pellet constituent percentage of pelts $\text{Cd/Te} \leq 1.0$ and $\text{Cd/Te} 1.0$). Both deposition temperatures and nitrogen pressure during deposition have been considered. From transmittance and reflectance measurements, the values of the absorption coefficient α , of the band gap E_g , have been calculated.

KEYWORDS: CdTe, Thin Film, Laser Ablatio

INTRODUCTION

Among many photovoltaic semiconductor materials used in solar cell fabrication, CdTe whose properties are well suited for this application, has come to the forefront, because of its direct band gap 1.5 eV at room temperature. This is optimum for a single junction solar cell at the AM1.5 solar spectrum. High absorption coefficient, only about a micrometer thick can absorb 90% of the solar spectrum (1).

This material has the ability to be doped with both (n) and (p) impurities and can be prepared by variety of preparation techniques [3–10]. For all these reasons CdTe based thin film solar cells are one of the leading candidates for low-cost, large-scale terrestrial photovoltaic applications. The calculated maximum theoretical efficiency of a single-crystal CdTe solar cell is close to 29 % (11), however, the best result for polycrystalline CdTe solar cells is about 16 % (12).

The conventional deposition techniques, employed so far, are associated with some disadvantages. These can be overcome by choosing laser evaporation technique due to the possibility of attaining a monolayer thickness control, enhanced film-substrate adhesion, compatibility with non contact masking techniques and minimum possible degradation [13, 14]. CdTe thin films, deposited by laser evaporation technique from single crystal, targets were reported by many workers in this field [15–18].

We have recently prepared thin lead telluride layers by a simple and cheap method using laser ablation of PbTe pellets pressed from high purity Pb and Te powders [19, 20]. The first aim of this paper is to study the correlation between physical properties of the CdTe films and their preparation conditions in order to have a comprehensive understanding of this correlation and for the improvement of the quality of these films for the technological applications.

The second goal is to highlight the influence of the pellet constituent percentage on the crystallographic, optical and electrical properties of the deposited films.

SAMPLE PREPARATION

Cadmium telluride films of different thicknesses (determined by using Newton interference fringes on the sharp edge of the films) were deposited in a vacuum chamber (230 mm in diameter and 250 mm height) under a residual pressure of 10^{-5} Torr. The system was equipped with a pulsed Nd: YAG laser operating at 1.06 μm wavelength, and 300 μs pulse duration with assorted optics. Both substrate and pellet holders were made from stainless steel.

The source holder was made to rotate after each pulse so as to expose a new position, keeping the source-substrate constant (4 cm). During the deposition, the laser beam was focused onto the target by a 20 mm focal length lens. The evaporation sources were pellets pressed from high purity powders (99.999%) with percentage range in weight of the constituent's cadmium and tellurium. The cost of preparation of a pressed pellet target is substantially lower than that of a target from a bulk crystal).

The crystallographic properties of deposited films were investigated by the X-ray diffraction technique using Cu K α radiation at scanning 2θ range of 20–1000. The targets used consist of pellet of both metals at different percentages, they crushed and cold-pressed several times before the final pressing. A fixed laser power density of $8 \times 10^5 \text{ W/cm}^2$ was used for deposition [densities below 10^6 W/cm^2 are usually classified under low power density range (21)]. In this range the particle's emission is expected to have the thermal character, in which the stream density S depends on the thermal energy kT acquired from the pulse energy).

Sheet resistance of deposited films were measured by a 4 - point probe using Veeco Instrument Model Fpp-5000. The absorption coefficients of CdTe between (450 – 900 nm) were obtained at room temperature using (λ -9) spectrophotometer. The UV reflectance spectrum was obtained by means of "Philips UV/ Visb spectrophotometer".

RESULTS

Structural Study

X-ray diffraction measurements were made in order to find the impact of deposition parameters on the CdTe film crystalline quality. Generally, deposited films with very sharp and intense peaks indicate highly crystalline nature with nearly stoichiometric composition. The X-ray diffraction data of five samples, figure (1), shows that the films are polycrystalline over the whole range of pellets compositions.

Besides, most of the prepared films exhibited predominant intense reflection peaks at approximately $2\theta = 32^\circ$ associated with (200) reflection, and exhibited lower intensity peaks in the (111) direction. Increasing cadmium percentage in the pellet showed a dramatic change in the x-ray diffraction spectra, as shown in the figure (?). The disappearance of (111) reflection was enhanced by higher cadmium percentage.

This may be attributed to the increased mobility of Cd atoms leading to some degree of growth control. The (200) texture was dominant throughout the deposition process as indicated from the intensity ratio of (111): (200) Bragg reflection. This suggests that the deposition from pellets with $40\% \leq \text{Te} \leq 60\%$ has no impact on the reaction in solid state between Cd and Te.

Furthermore, increasing the Cd percentage in the pellet did not allow additional Cd peaks as shown in the diffractogram of figure. The height of the (0 0 2) peak relative to other reflection signifies the extent of c-axis orientation and film structural quality.

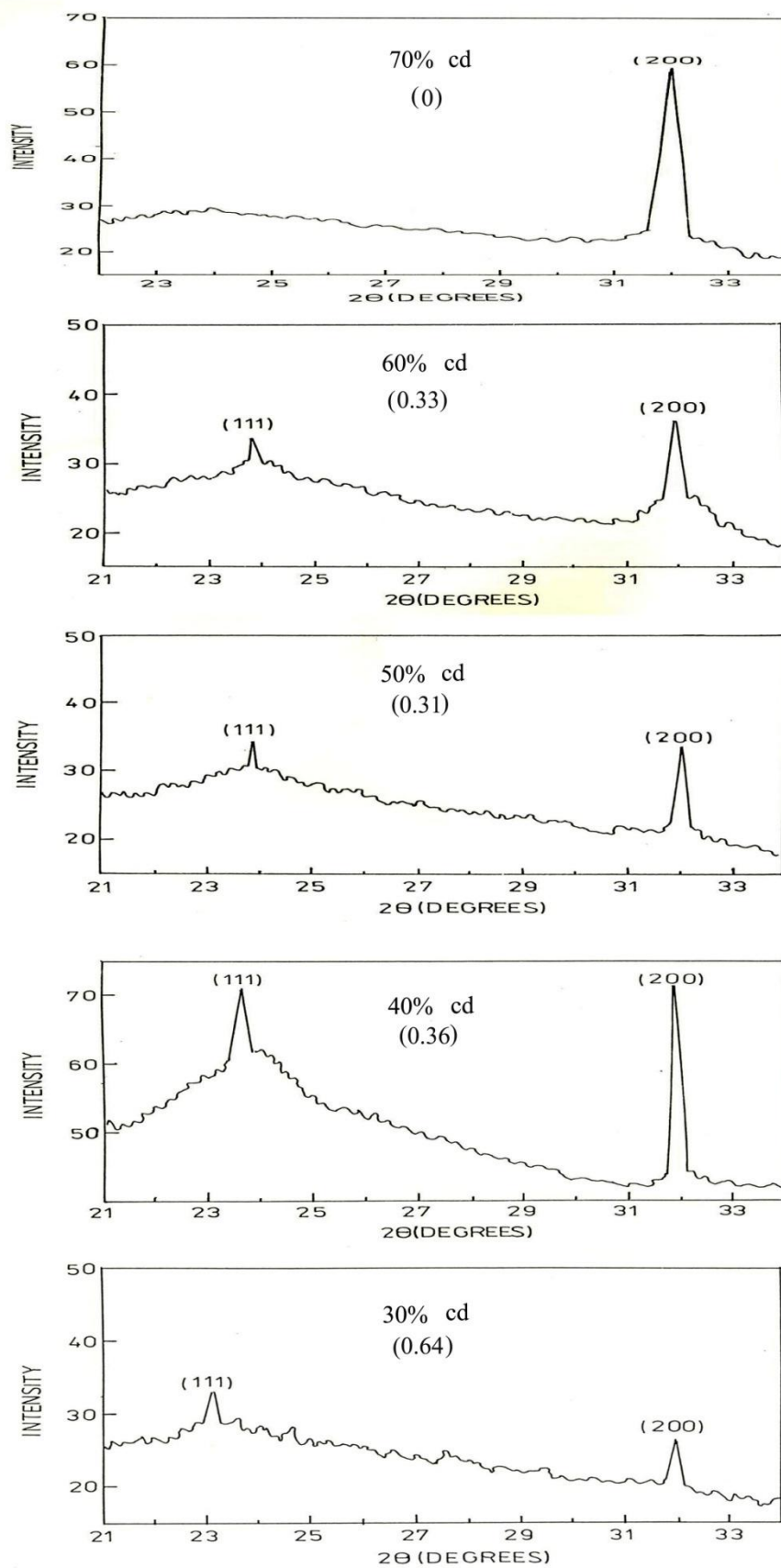


Figure 1: X-ray Diffraction of Deposited thin Films Grown from Pellets of Different Cadmium Percentage

OPTICAL PROPERTIES

Optical Transmission

The 0.4–3.2 μm transmission range of the CdTe films prepared on substrates from stoichiometric and non-stoichiometric pellets is presented in figure (2). A steep increase in transmission takes place at the wave length 0.8 μ (1.55 eV). The highest transmission is that of a film deposited from 40 % Cd. Also, the spectral transmission has decreased with increasing the Cd percentage. Transmission curves belong to films deposited from pellets with 30% or 70% of either element shows a different trend where the steep increment was vanishing.

This results because these films are no more CdTe films. The UV reflectivity curve of samples prepared from stoichiometric pellet showed the lowest values as depicted in figure (3). The curves show a peak close to 240 nm and a wide band at 280–320 nm. A third band at 368 nm is also probable. In the investigated wavelength range, the results are close to those previously reported for thin polycrystalline CdTe films (22) and confirm the good optical quality of deposited films in the current study. The third peak disappeared in films deposited from pellets with 30% or 70% Cd.

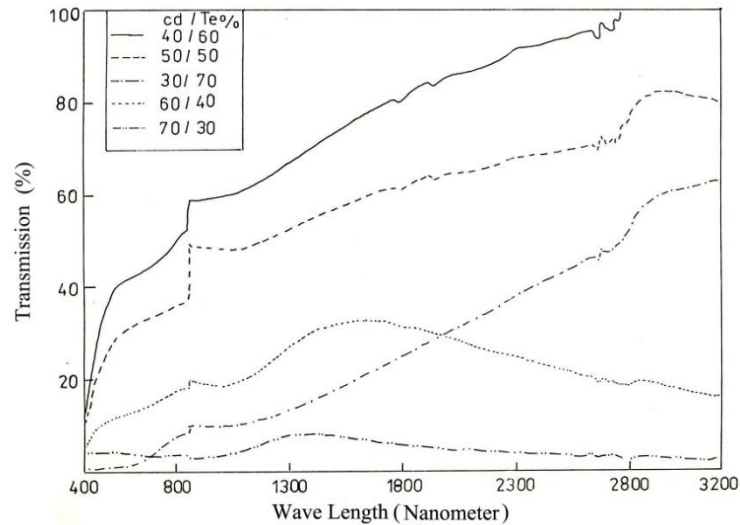


Figure 2: Transmission Spectra of CdTe Films Deposited Film from Different Pellets Percentage

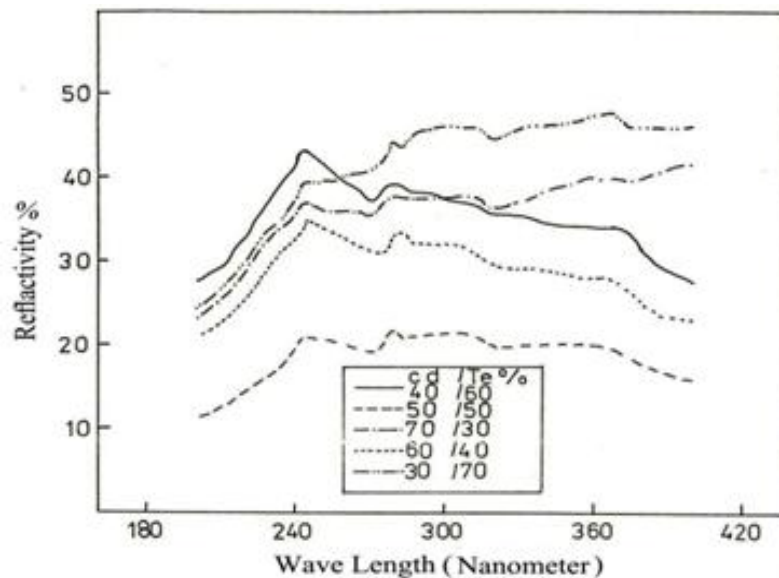


Figure 3: UV Spectral Reflectivity of Deposited Films from Different Pellets

Absorption coefficients (α) were deduced from the transmission and reflection measurements. The variation of (α) as a function of incident photon wavelength for different compositions is shown in figure (4). It is clear that the value of the absorption coefficient (α) increases with increasing the photon energy and was found to exhibit a strong compositional dependence. For Cd at 60 %, the absorption coefficient had the highest value of absorption and remained nearly constant as photon energy increases. A sudden decrease in the absorption coefficient was noticed for other values of Cd percentages. This may be due to the changes taking place in the bonding arrangement as a result of pellet compositional changes (23).

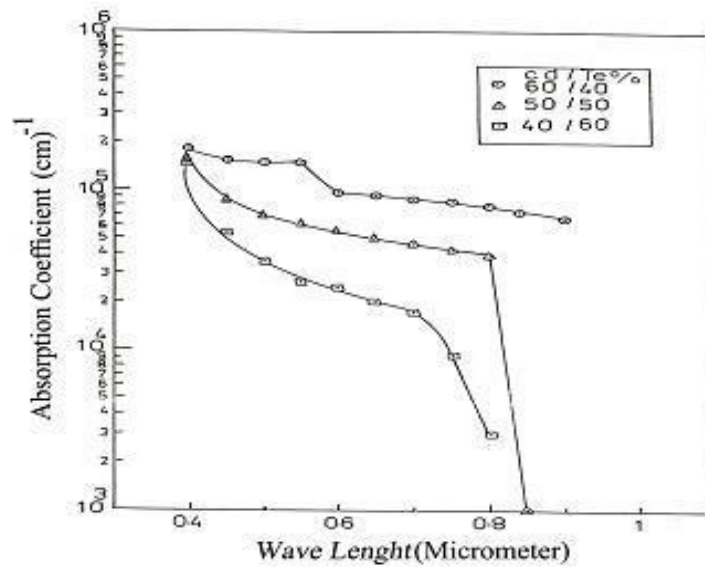


Figure 4: Dependence of Absorption Coefficient on Cd percentage

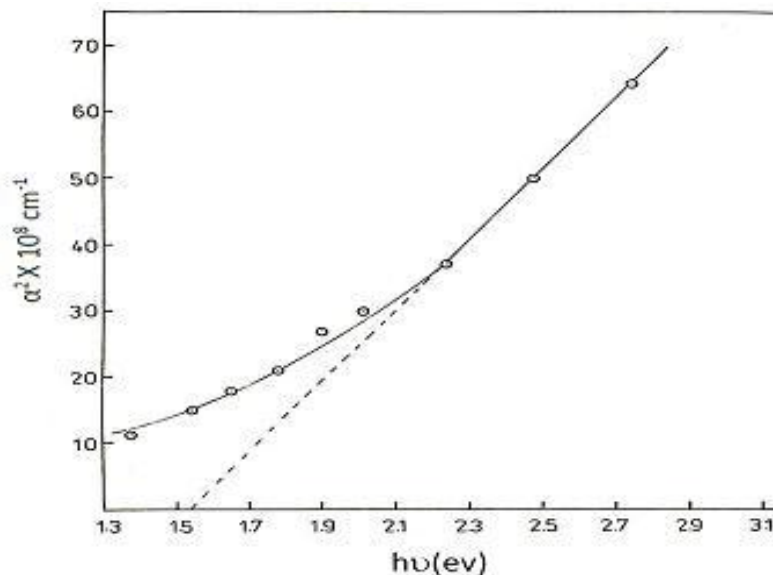


Figure 5: Band Gap of Film Deposited from Pellet with 50% Cd

The experimental results for the prepared $\text{Cd}_x\text{Te}_{1-x}$ thin films at different compositions has allowed direct transitions to occur as shown in figure (5). Optical band gaps for different Cd x Te 1-x films were estimated from the intercept of the straight lines obtained at zero absorption ($\alpha = 0$). Their estimated values were between 1.35 – 1.55 eV depending on the pellet percentage. Furthermore, the value of the direct optical gap increased with increasing the metallic percentage concentration of Cd.

Electrical Properties

Table (1) reports the evolution of the CdTe sheet resistance as a function of pellet stoichiometric for films deposited by evaporating stoichiometric and non stoichiometric pellets pressed from high purity (99.999%) powders of the constituent elements. Using different percentage pellets, films' sheet resistance decrease with increasing cadmium percentage. Films have been turned into n-type and the resistivity decreased when further increase of the Cd percentage ($\geq 50\%$) was allowed. Such dependence of $[R_{\square}]$ with Cd % can be explained either by the changes in the degree of non stoichiometric of the CdTe pellet constituent or by increasing the donor impurities. The latter occurred in the CdTe at higher Cd percentage; as Cd plays the role of donor impurity (24). Samples with 70% Cd was not counted for comparison since they showed different trend in UV reflection (i.e. they were no more CdTe). For Cd percentage of $\leq 40\%$, conductivity type could not be determined although the as-deposited layers were preferentially p-type, and that n-type doping could be obtained by adding more Cd in the layers. The high value of sheet resistance accompanied the 50 % Cd samples could have resulted from the compensation effect that took place. Table (1) shows also that the Cadmium concentration, corresponding to full compensation, is between 40-50%.

Table 1: Sheet Resistance as a Function of Percentage of the Pellet Constituent's Cadmium

Sample	Cd%(Cd / Te)	Sheet Resistance /cm ² Ω	Conductivity Type
S1	30 \approx (0.43)	3440	-
S1	40 \approx (0.66)	1550	-
S3	50 \approx (1)	968	n-type
S4	60 \approx (1.5)	28.8	n-type
S6	70 \approx (2.33)	10.5	n-type

DISCUSSIONS

From the X-ray diffraction experiments performed when varying the percentage of pellets constituents, it can be inferred that in the range of 40%-60%, CdTe films nucleate with a preferential orientation along the (2 0 0) plane. Increasing the cadmium percentage has increased the intensity of peaks corresponding to the lead (1 1 1) plane. It can be noticed that preparation of films using pellets containing an excess of Cd has permitted preferential grow of the (2 0 0) plane and the suppression of the (1 0 0) direction.

For equal Cd and Te percentage in the pellets, transmission and reflection showed results in good agreement with the previous ones. A drastic change was observed with 30% and 70% percentage pellets. UV reflectivity measurements indicated crystalline structure only appears at 40-60% percentage. Increasing the cadmium percentage leads to a destruction of the structure, a result that agrees well with the XRD findings. Similar results were obtained for the absorption coefficient.

The electrical results obtained for the layers as a function of pellet composition are briefly discussed in the following. First, the resistivity increase of the deposited layers with increasing pellet's non-stoichiometry can be attributed to structural changes in the layers. Increasing the cadmium percentage in the pellets produces a decrease in sheet resistance, indicating a compensation effect. This result is in agreement with the fact that the as-deposited layers are preferentially p-type and that n-type doping can be obtained by adding more Cd in the layers. The sheet resistance

decreases by a factor of 50 times when increasing the Cd percentage from 40% up to 60%. As cadmium acts as a donor in CdTe, the sheet resistance decreases again because of the compensation effect.

CONCLUSIONS

We have shown the possibility of preparing thin films of CdTe using laser ablation of pressed pellets prepared from cadmium and tellurium powders. Equal Cd and Te percentages in the pellets produce thin films of optical and electrical properties comparable to those of films obtained by other methods. PLD of variable percentages of pellets constituents showed a meaningless influence on the ratio of the two diffraction planes. On contrary, increasing the cadmium percentage produces notable effects on them. A right conjunction of pellets percentage would improve the structural properties and make the energy band gap close to 1.5 eV. The optical properties of ablated films are well fitted to the bulk material. CdTe films have been considered as compensated semiconductor containing acceptor level located near the valance band and donor level near the conduction band. Films with rich Te are dominated by the acceptor level, while donor level will dominate the Cd rich films. We have deposited P- and n-CdTe films by deviation of the evaporated source from the stoichiometry. Donor doping can be achieved by the introduction of more cadmium which also gives n-type doping. The Sheet resistance was varied between 3440 and 29 Ω / cm^2 depending on the pellet composition. This means a control of resistivity is achieved by the changing the pellets composition.

REFERENCES

1. V.A. Gnatyuk , T. Aoki, O.I. Vlasenko , S.N. Levytskyi , B.K. Dauletmuratov, C.P. Lambropoulos ; Applied Surface Science 255 (2009) 9813
2. E. Saucedo, O. Martínez, C.M. Ruiz, O. Vigil-Galán, I. Benito, L. Fornaro, N.V. Sochinskii, E. Diéguez; J. Cryst. Growth 291 (2006) 416.
3. Chen Huimin, Guo Fuqiang, and Zhang Baohua; Journal of Semiconductors Vol. 30 (2009) 053001-1
4. Murat BAYHAN ; Tr. J. of Physics 22 (1998) , 929
5. T.M. Razykov, R. Acher, O.D. Crisalle, V.Craciun, T.J. Anderson, K. Kouchkarov, S.S. Li, D.Y. Goswami S. Vijayaraghavan ; IEEE Photovoltaic Specialists Conference 2005,484-486.
6. Ye.O. Bilevych, A.I. Boka, L.O. Darchuk, J.V. Gumenjuk-Sichevska, F.F. Sizov, O. Boelling and B. Sulkio-Cleff ; Semiconductor Physics, Quantum Electronics & Optoelectronics. V. 7, (2004). P. 129-132.
7. A U Ubale, R J Dhokne, P S Chikhlikar, V S Sangawar and D K Kulkarni; Bull. Mater. Sci., Vol. 29, No. 2, April 2006, pp. 165–168.
8. X. Mathew, J. Phys. D: Appl. Phys. 33, 1565 (2000).
9. R. K. Sharma, G. Singh, A.C. Rastogi, Sol. Energy Mater. Sol. Cells 82, (2004). 201.
10. Chen Huimin, Guo Fuqiang;, and Zhang Baohua ; Journal of Semiconductors 30, (2009) 053001 .
11. A. W. Brinkman, Properties of Narrow Gap Cadmium-Based Compounds, edited by P. Capper ~IEE., London Vol. 10 (1994), 591.
12. T. L. Chu and S. S. Chu, Solid-State Electron. 38, (1995) 533.
13. x. zeng z.wang, y. liu, m. ji ; Appl. Phys. A 80, (2005) 581–584.

14. R. Cristescu, D.Mihaiescu, G. Socol, I. Stamatina, I.N. Mihailescu, D.B. Chrisey ; Appl. Phys. A 79, (2004) 1023–1026.
15. J.J.Dubowski and D.F.Williams; Appl.Phys.Lett Vol.46 (1985)1081.
16. F. de Moure-Flores, J. G. Quiñones-Galván, A. Guillén-Cervantes, J. Santoyo Salazar, A. Hernández-Hernández, M. de la L. Olvera, M. Zapata-Torres, and M. Meléndez-Lira; AIP ADVANCES 2, (2012) 022131.
17. V.Montgomery and J.H.Dinair ; Thin Solid Films 124 (1985) 462.
18. Yu.A.Bykouski , A.G.Dudoladov and P.Kozlenkov ; Sov. Tech.Phys.Lett 11 (1985)540.
19. A.M. Mousa, J.P. Ponpon, Eur. Phys. J. Appl. Phys. 34 (2006) 1.
20. Ali M. Mousa, J.P. Ponpon ;, Applied Surface Science 254 (2007) 1215–1219
21. Cheung J. T. &.Sankur, H.,Critical Rev. Solid St. Mat. Sci. 15, (1988) 63–109
22. J.T.Cheung and M.Khoshnevisan; Appl.Phys.Lett.; 43 (1985) 462.
23. K.L. Bhatia, M. Singh, N. Kishore, Thin Solid Films 293 (1997) 303.
24. M.takahashi,K.Uosaki and h.Kiata ; J.Appl.Phys. 60 (1988) 2046.